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Optical dephasing by uncorrelated phonon scattering to librations. An optical and picosecond photon echo study of a photosite of pentacene in benzoic acid

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We report results of an optical and picosecond photon echo study on the zero-phonon line of photosite I of pentacene in benzoic acid. The results show that optical dephasing in this system proceeds via uncorrelated phonon scattering processes from the ground and optically excited state to singly excited librational levels. It is also shown that the data can not be consistently interpreted using coherence exchange theory. The librational frequencies and lifetimes at low temperature are determined to be 12 cm^{-1} and 18 ps in the ground state and 16.7 cm^{-1} and 2.5 ps in the singlet excited state. It is argued that population decay of librational overtones proceeds in single quantum steps down the librational ladder which excludes these modes from playing a role in optical dephasing. From a temperature-dependent line shape study of the libronic transition in absorption, it is concluded that the low-temperature librational lifetime is primarily due to resonant decay into acoustic phonons. At elevated temperature, cubic libration-phonon anharmonicity dominates the librational lifetime. These lifetime shortening processes are reflected in the temperature dependent dephasing of the origin. Finally, with the dephasing model presented in this paper for photosite I, existing controversies concerning optical dephasing in the unburned origin of pentacene in benzoic acid can be resolved.

I. INTRODUCTION

McClure[1] was the first one to recognize that many of the sharp peaks in the phonon sideband structure of electronic and vibronic spectra in mixed crystals are transitions that involve librations of the guest molecule in a cage of host molecules. In the specific case of the naphthalene-in-durene mixed crystal he suggested that a 18 cm^{-1} phonon peak observed in the lowest excited singlet state is due to a naphthalene libration around the out of plane axis. This suggestion was recently confirmed in a Monte Carlo type calculation of the librational potential for this naphthalene motion by Koehler and Schmidt.[2] McClure further noted that this libration in the naphthalene spectrum also acted as a "false" origin which indicated that this libration is highly localized at the guest site.

It was more than a decade later that, through spin echo,[3] photon echo,[4] and photochemical hole burning[5] experiments, it became clear that these guest librations play a crucial role in the spin-, Raman-, and optical-dephasing processes that determine the homogeneous line shape. Following van't Hof and Schmidt,[6] several theories have been advanced[7-11] to explain the observed quasiexponential activation of the low-temperature homogeneous linewidth of these transitions. Völker *et al.*[5] showed that in the case of free base porphin doped into Shpol'skii host crystals, *exchange theory* quite nicely explains the observed optical linewidth and shift with increasing temperature. Wiersma and coworkers claimed that in many chemically mixed crystals[12] *uncorrelated phonon scattering* in the ground and excited states determines optical dephasing. De Bree and Wiersma (dBW)[10] recently presented a detailed microscopic theory of optical dephasing using a four-level system coupled to an anharmonic phonon bath where next to the ground and electronically excited state the lowest frequency libration in each state was "projected out" of the phonon bath.

From this theory it became clear that coherence exchange and uncorrelated phonon scattering (UPS) are limits of a more general relaxation theory, coined by de Bree and Wiersma as optical Redfield theory. They further emphasized that exchange of coherence between the cold and librationally hot transition can only occur when these transitions spectrally overlap. On optical (electronic) excitation the librational potential may undergo substantial changes as noted by McClure[1] and explained by Koehler and Schmidt[2] as resulting from a change in molecular geometry. It is therefore expected that these "exchange conditions" are more likely to be met for spin and Raman than for optical transitions. A striking illustration of this point was recently presented by Duppen *et al.*[13] in a comparative study of vibrational and vibronic dephasing in pentacene doped into naphthalene. Raman dephasing within the electronic ground state manifold was shown to be ineffective due to *coherence exchange* between the cold and librationally hot vibrational transition. In contrast, vibronic dephasing, involving the *same* libration, increased rapidly with temperature through UPS processes in the initial and final state. It therefore seems that the dBW theory of optical dephasing in a crystalline environment gives a satisfactory description of the results obtained. However, what presently is lacking is a *clear* demonstration of the biexponential activation of the homogeneous linewidth as required by the UPS mechanism and a direct measurement of the (temperature dependent) lifetimes of the librational modes which are, in addition to the librational frequencies, the essential parameters in both exchange and uncorrelated phonon scattering (dBW) de-

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phasing theory. Moreover, the dBW theory is basically a four-level theory and therefore does not include the effects of overtones of the active libration, nor does it incorporate contributions of the other guest librations to the homogeneous line shape. As complete verification of the Redfield- UPS limit necessitates dephasing measurements up to temperatures where population of these other modes no longer can be neglected ($\sim$20 K), a further study of optical dephasing in mixed molecular crystals was deemed necessary.

In a recent paper by Duppen *et al.*,[14] results of ps photon echo experiments on pentacene in benzoic acid were reported. These results seemed to indicate that next to librational dephasing, involving a libration of 16.5 cm^{-1}, adiabatic coupling to acoustic host phonons[15] was also of importance in this system. This conclusion was drawn on the basis of comparison of the phonon sideband in absorption and emission which both seemed to have a progression in a 16.5 cm^{-1} mode. In a later paper by Olson *et al.*[16] results of low-temperature photochemical hole burning experiments indicated that, up to 5 K, the homogeneous linewidth increased exponentially with temperature with an activation energy of 11 cm^{-1} and preexponential constant of 0.3 cm^{-1}. Andrews and Hochstrasser[17] concluded from a coherent Stokes Raman scattering study that the homogeneous line shape was activated with an energy of 13.8 cm^{-1}. In view of these controversies it seemed worthwhile to reinvestigate this system.

Here the photon echo experiments are extended to a photosite of pentacene in benzoic acid. When pentacene in benzoic acid is excited to its electronically excited state, proton rearrangements in the host occur that lead to the appearance of several metastable pentacene sites[16] in the crystal.

We have performed echo experiments on the most red shifted photoinduced pentacene site (I) for the following reasons: First, in contrast to the unburned origin, this site shows a distinct progression in a 16.7 cm^{-1} libration. Furthermore, the intensity of the fundamental libronic transition is such that photon echo experiments on this band seemed feasible, which is important in a direct determination of its lifetime. Finally, the fluorescence spectrum of this site shows more pronounced structure than that of the unburned origin which is essential in assigning the librational mode in the ground state.

The results presented in this paper show that the UPS limit of the dBW theory correctly describes the homogeneous line shape of this site up to 20 K, where the homogeneous linewidth exceeds the low-temperature limit by a factor of 10^4. The librational frequencies in the ground and excited states are determined to be 12 and 16.7 cm^{-1} with low-temperature lifetimes of 18 and 2.5 ps, respectively. It is further shown that the low-temperature lifetime of the libration in the excited state is mainly due to direct decay into acoustic phonons at the same frequency. At higher temperature, phonon up- and down-conversion processes reduce the librational lifetime.

Finally, it is concluded from the great similarity between the dephasing of photoinduced site I and the unburned origin that the same dephasing mechanism holds for both transitions, which resolves existing controversies.

II. THEORETICAL BACKGROUND

In order to understand the significance of the results presented in Sec. IV, it is necessary to introduce the optical level scheme shown in Fig. 1. Here $|1\rangle$ is the ground state and $|2\rangle$ the electronically excited state of the isolated guest impurity molecule in the host lattice. Levels $|3\rangle$ and $|4\rangle$ are associated with librations of the guest molecule in the ground and excited states. The other heavy drawn lines in the figure indicate two- and three-quantum excitations of these librations. The levels $|k\alpha\rangle$ are acoustic phonons of branch α with wave vector $\mathbf{k}$. We note that higher quantum excitations and other molecular librations have been omitted. Several types of interactions take place between the four prominent levels and the lattice phonon bath. The total effect of these perturbations on the homogeneous linewidth $(\pi T_2)^{-1}$ of the zero-phonon line (the transition $|2\rangle \leftarrow |1\rangle$) can be expressed by the following well-known relation:

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1}, \tag{1}$$

where T_1 represents the excited state fluorescence lifetime and T_2^* the pure dephasing time constant which is determined both by pure dephasing and phonon-induced population relaxation effects within the four-level system. Using Redfield theory de Bree and Wiersma[10] calculated the effects of the different perturbations on the homogeneous line shape. For the present discussion we will focus on the dominant contribution, the diagonal quadratic electron-libration coupling, to the line shape, which in the UPS limit (*vide infra*) becomes

$$\frac{1}{T_2^*} = \tfrac{1}{2}(\tau_3^{-1}(T)e^{-\hbar\omega_{31}/kT} + \tau_4^{-1}(T)e^{-\hbar\omega_{42}/kT}), \tag{2}$$

where $\tau_3(T)$, $\tau_4(T)$ and ω_{31}, ω_{42} are the temperature-dependent lifetimes and frequencies of the librations in the ground and excited state, respectively. We safely assume here that intersystem crossing and internal conversion do not contribute to τ_4 in pentacene. Note further that in this expression there is no sum over multiple quantum excitations of the

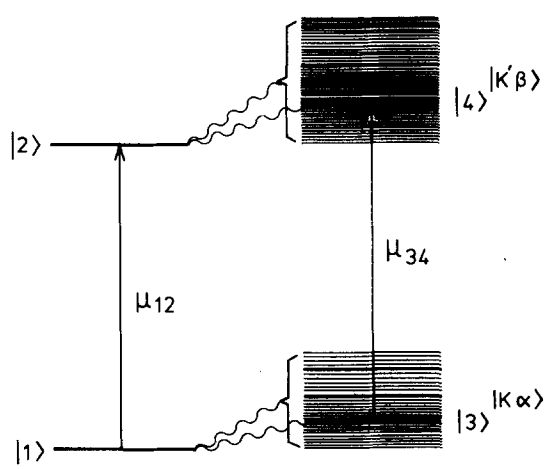

FIG. 1. Level structure of an optical transition $|2\rangle \leftarrow |1\rangle$ interacting with pseudolocalized librational levels $|3\rangle$ and $|4\rangle$, and delocalized crystal states $|k\alpha\rangle$ and $|k'\beta\rangle$.

libration. In Sec. IV E we will discuss this point. It is also important to realize here that the UPS process involves population relaxation processes *within* the four level system of Fig. 1. We choose however, in accordance with existing literature,[10] to account for these processes in the T_2^* part of Eq. (1), as they cause the broadening of the transition of interest (i.e., transition $|2\rangle \leftarrow |1\rangle$). With this interpretation T_2^* comprises both adiabatic and nonadiabatic processes.

De Bree and Wiersma also showed that in the special case where the cold (optical) and librationally hot transition overlap *and* the lifetime of the libration in ground and excited state is identical, the well-known effect of exchange of coherence between these transitions may occur. In this case the contribution to the dephasing parameter becomes

$$1/T_2^* = \frac{\delta^2 \tau}{1+\delta^2\tau^2} e^{-\hbar\bar{\omega}/kT}, \tag{3}$$

where $\bar{\omega} = \frac{1}{2}(\omega_{31} + \omega_{42})$ is the average librational frequency and τ the lifetime of the libration, which is necessarily identical in ground and excited states in this formalism. While this equation strictly only holds[10] for $\delta\tau \lesssim 1$, where δ (in rad/s) presents the frequency difference between the transitions that undergo exchange, it has also been applied in the limit where $\delta\tau > 1$ ("slow exchange"). The difference between the UPS and exchange limits of the Redfield relaxation theory is clear from a comparison of Eqs. (2) and (3). In the UPS limit, the homogeneous line shape broadens with temperature as a sum of two exponents, while in the exchange limit single exponential activation is required. In the case of a quasiexponential activation of the linewidth, knowledge of the lifetime of the libration in the ground and/or excited states enables a proper choice of the dephasing mechanism. It is further important to note that when the librational frequencies and their temperature-dependent lifetimes are known, no freedom is left in predicting the broadening of the homogeneous line shape arising from the quadratic electron-libration coupling.

In the intermediate case where one of the exchange conditions is not met, the line shape function is more complex and for this case we refer to Ref. 10, where a detailed discussion of all aspects of optical Redfield relaxation theory is given. Here also the effects of adiabatic coupling to the band phonons are discussed, which would lead to a T^7 dependence of the homogeneous linewidth.

III. EXPERIMENTAL

Single crystals of pentacene in benzoic acid were grown by the Bridgman method from zone-refined benzoic acid doped with pentacene obtained from Fluka. The final concentrations of pentacene in benzoic acid were in the range of 10^{-4}–10^{-5} mol/mol. After cleaving the crystals from the boule, by using a razor blade, they were mounted in a temperature-variable cryostat built by Oxford Instruments.

In all experiments, photosite I of pentacene in benzoic acid was generated by irradiating the mixed crystal with an argon laser operating at 5145 Å. In the photon echo experiments a steady state concentration of photosite I high enough to perform the experiments was obtained by irradiating the crystal with 500 μW of argon laser light. The echo-exciting laser beams and the argon laser beam were focused on the same 100 μm spot of the crystal. Total dye-laser power was kept at or below 800 μW. In case of photon echo experiments on the phonon sideband, 2 mW of argon laser light was used and it was checked that by lowering the intensity of the argon laser no change in the measured echo decay was observed. A schematic of the setup used to generate the accumulated photon echoes is shown in Fig. 2. The echo experiments were further performed as described in Ref. 18.

The fluorescence lifetime of pentacene in site I was measured by excitation with a nitrogen-pumped dye laser and display of the fluorescence signal on a Tektronix transient digitizer. Reabsorption of the fluorescence signal was kept to a minimum by using crystals of only 10% absorption.

IV. RESULTS AND DISCUSSION

A. Absorption and emission spectra

Figure 3(A) shows the absorption spectrum of photosite I of pentacene in benzoic acid at 1.5 K. The underlying solid

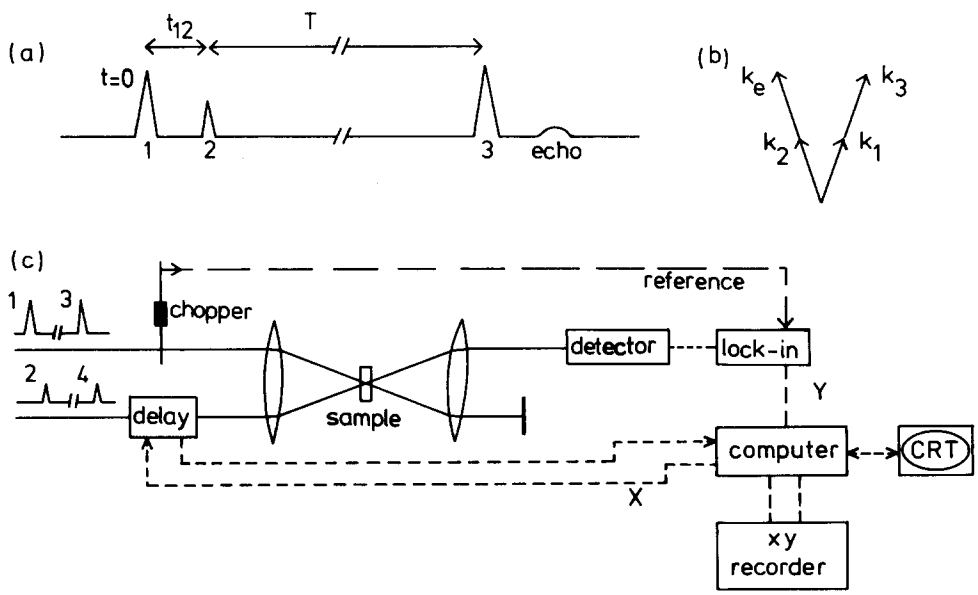

FIG. 2. Schematical setup for the generation and detection of accumulated photon echoes. (a) Excitation pulse cycle; t_{12} is the variable delay time between the excitation pulses and T the fixed cycle time. (b) Phase-matching diagram of the excitation pulses and echo. (c) Setup for detection of intensity modulations on the probe beam (2 and 4) from modulation of the pump beam (1 and 3). An Apple II computer steps the delay t_{12} between the excitation pulses and also digitizes the incoming signals from the lock-in amplifier.

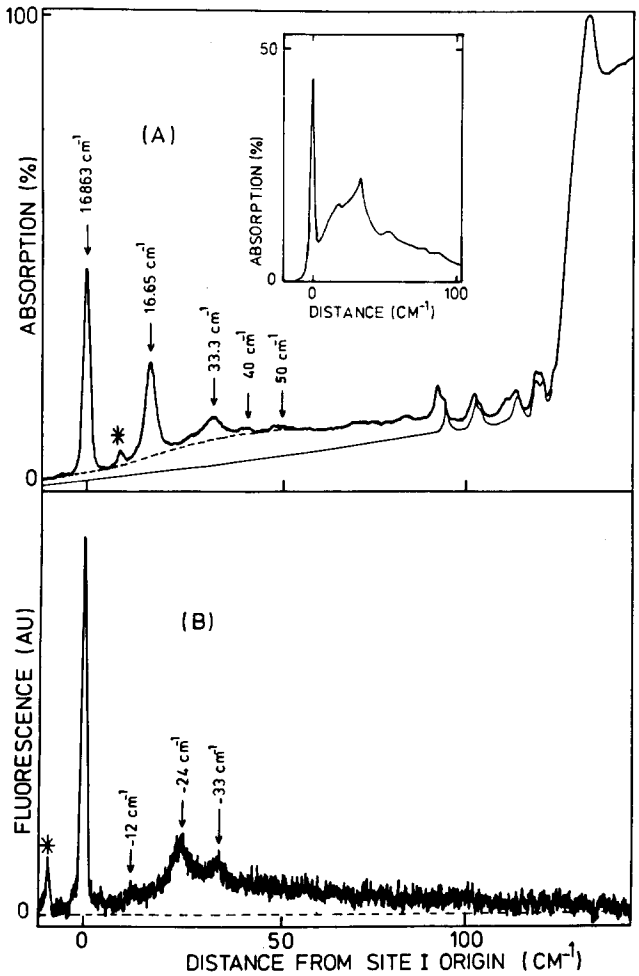

FIG. 3. Absorption (A) and emission (B) spectra of photosite I of pentacene in benzoic acid at 1.5 K. To facilitate comparison between the two spectra we have used an increasing wave number scale in Fig. 3(A) and a decreasing scale in Fig. 3(B). Asterisks mark the position of the zero-phonon line of site V (cf. Ref. 16). The intensity of this peak was used in emission to calibrate the intensity of the zero-phonon line of site I. The insert in Fig. 3(A) shows the absorption spectrum of the unburned origin in a crystal where the concentration is such that the optical density at the origin is identical to that of site I in Fig. 3(A).

line in the spectrum presents the absorption of the sample, before proton rearrangement has occurred. It is clear that next to the existence of well-defined sites also a broad absorption is generated in the rearrangement process. The dotted line in the spectrum indicates what we believe is the true absorption background of photosite I. The starred absorption is due to photosite V.[16] Taking this into account we calculate for photosite I a Debye–Waller factor $(I_{zpl}/(I_{zpl} + I_{psb}))$ of 0.49 ± 0.03. Here I_{zpl} is the intensity of the zero-phonon line and I_{psb} the integrated intensity of the phonon sideband. The insert of Fig. 3(A) shows the absorption spectrum of the unburned origin at low temperature. Comparison of the two spectra shows a considerable difference in phonon sideband structure indicating a noticeable change in electron–phonon coupling after proton rearrangement. This is also reflected in the Debye–Waller factor for this transition which is only 0.16.[19] Figure 3(A) further shows that the photosite spectrum exhibits a clear progression in a 16.7 cm^{-1} mode. This mode, previously noted by Olson *et al.*,[16] is assigned by us as the lowest-frequency librational mode of electronically excited pentacene in this site. From the intensity distribution in the librational progression we calculate[20] a reorientation angle of 1.3° along this coordinate. Note that in the unburned origin the same mode is observed but with a different intensity pattern and riding on a much more intense background absorption. In the photosite spectrum we further discern an absorption at 40 cm^{-1} from the origin which may be due to another librational mode of pentacene. Monte Carlo calculations of the type reported by Koehler[21] are presently in progress to investigate this idea. Figure 3(B) shows the emission spectrum of photosite I after excitation with a cw dye laser in the librational absorption. Note that the relative intensity of the origin, after correcting for reabsorption, is four times greater than presented. This shows that in emission the intensity in the librational bands is far less than in absorption. However, we clearly observe a progression in a 12 cm^{-1} mode and assign this mode to the lowest-frequency libration of pentacene in the ground state. The feature at 33 cm^{-1} from the origin may correspond to the 40 cm^{-1} peak observed in the absorbed spectrum. As stated before, in emission much of the intensity in the phonon sideband is found in the acoustic phonons at higher frequency; a possible reason for the nonobservation of this ground state mode by Olson *et al.*[16] It is gratifying to note that the Debye–Waller factor in emission is found to be 0.51 ± 0.03, within experimental error identical to the one in absorption. This fact lends credence to our choice of baseline in the absorption spectrum as discussed above.

What remains to be understood is the dramatic difference between the phonon sideband in absorption and emission of this site. While in absorption all the intensity is found in a librational progression, in emission most of the intensity is found in the acoustic modes. An interpretation of this effect in terms of a "Duschinsky"-type mixing, allowed by the loss of inversion symmetry of this site, is underway.[22]

The most important conclusion pertinent to this work is that in photosite I the lowest-frequency libration of pentacene is 12 cm^{-1} in the ground state and 16.7 cm^{-1} in the excited state. An attempt to observe, at higher temperature, a hot band at 4.7 cm^{-1} to the blue of the origin was inconclusive due to the fact that at higher temperatures ($\gtrsim 4$ K) new spectral features arise due to thermally activated proton rearrangements in the host crystal.

B. Librational lifetime

As was pointed out in Sec. II, next to knowledge of the librational frequencies, the lifetimes of these modes need to be known in order to predict theoretically the dephasing characteristics of the pure electronic transition. The first *direct* measurement of a librational lifetime was recently made by the Völker group,[23] on the system free-base porphin doped into *n*-decane, using the photochemical hole burning technique. For the 5.6 cm^{-1} libration in the excited state they obtained from the hole width a lifetime of 115 ± 20 ps.

To measure the excited state librational lifetime of site I of pentacene in benzoic acid we have performed accumulated photon echo and line shape experiments. Figure 4(B)

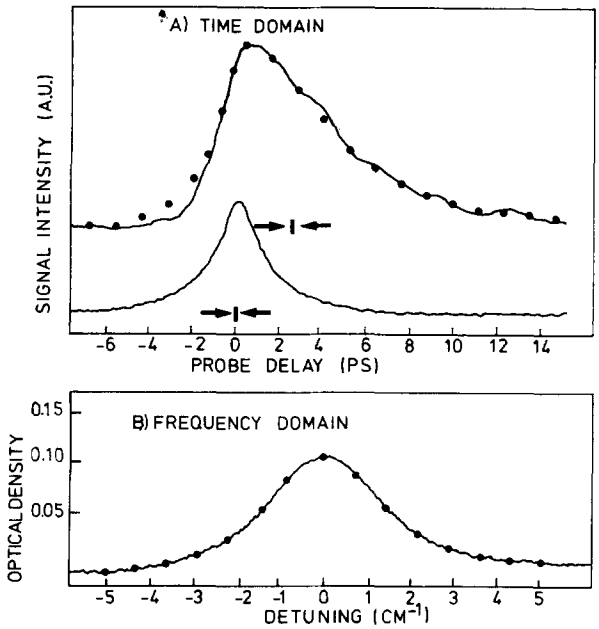

FIG. 4. Determination of the librational lifetime. (A) In the time domain from decay of the photon echo (upper trace). The lower trace represents the autocorrelation of the excitation pulses. The vertical bars represent the position of the intensity-weighted time average of both signals (see the text). (B) In the frequency domain from a line shape analysis of the libronic transition. The dotted fits in A and B are discussed in the text.

shows on an expanded scale the line shape of the fundamental librational transition at 1.5 K. It is clear that the line shape is very close to being Lorentzian. If we assume that the underlying inhomogeneous width is identical to that of the origin we calculate a homogeneous width of 2.2 cm^{-1} for this librational transition which corresponds to a librational lifetime of 2.4 ps. The dots in Fig. 4(B) correspond to points of the simulated Voigt line shape with an inhomogeneous width of 1.0 cm^{-1} and a homogeneous width of 2.2 cm^{-1}. As this librational lifetime is of essential importance in the analysis of our results we decided also to directly attempt to measure this lifetime using the technique of accumulated photon echoes. Figure 4(A) shows the result of such an echo experiment together with the autocorrelation of the excitation pulses. By deconvoluting the correlation signal with an exponential decay curve with a decay constant of 2.5 ps the dots in Fig. 4(A) are generated. The fit is excellent except at the rising edge of the signal. The discrepancy here is ascribed to excited state absorption of pentacene. Another way of determining the decay time is to calculate the intensity-weighted time average of both the autocorrelation and the echo signal. One can show[24] that in case of a symmetrical impulse function and exponential decay of the system's response, the time difference between these averages equals the decay parameter of the response function. With this method we also calculate a decay time of 2.5 ps. We therefore conclude that the lifetime of the libration in the excited state equals 2.5 $\pm$ 0.1 ps.

The excellent agreement between the librational decay time as obtained from a line shape analysis and photon echo decay also shows that the inhomogeneity in the librational transition is identical to that of the origin. Thus a line shape analysis of the librational transition at higher temperature should lead to an accurate measurement of the underlying homogeneous linewidth. In Sec. D the temperature dependence of this linewidth will be discussed.

As will be obvious from Fig. 3(B) it is impossible to measure the librational lifetime in the ground state from the fluorescence spectrum. In principle, it would be possible to measure this lifetime by doing multiresonant time-resolved CARS experiments.[25] Because of the weak oscillator strength of the fundamental librational transition in emission, we have not attempted to perform such an experiment. Direct measurement of this lifetime therefore is presently out of reach but an *indirect* determination is possible once the question of the appropriate dephasing mechanism is settled.

C. Temperature dependence of the homogeneous linewidth of the zero-phonon line of photosite I

In order to determine the temperature dependence of the homogeneous linewidth of the zero phonon line of photosite I we have performed photon echo and linewidth measurements. An example of an accumulated photon echo decay is given in Fig. 5 where it should be noted that the steady state concentration of photosite I in these experiments is such that the absorption strength at the origin corresponds to an optical density of only 0.02. The pure dephasing contribution to the homogeneous linewidth obtained from these echo decays is presented in Fig. 6 by the open squares. These experimental points, $(\pi T_2^*)^{-1}$ in cm^{-1}, were obtained from the photon echo decay time (T_2) by subtraction of the lifetime (T_1) contribution using Eq. (1). At temperatures below 4 K this method becomes impractical because of the long scanning times and other experimental problems. At these temperatures we have therefore inferred the echo decay times from a measurement of the echo intensity as a function of temperature at a fixed delay. An example of such a run is given in Fig. 7 together with a fit to be discussed later. The data points obtained from these runs are indicated by filled dots in Fig. 6. Finally, at temperatures above 15 K linewidth measurements were performed and the homogeneous linewidth extracted by deconvoluting the known inhomogeneous linewidth at low temperatures from the Voigt line shape. These data points are indicated by open circles in Fig. 6.

Up to 20 K the fluorescence lifetime of pentacene in site I was measured to be 23 $\pm$ 1 ns and independent of temperature. Since we measured the fluorescence lifetime using a crystal with 10% absorption at the origin of site I, the measured decay time may have been slightly influenced by reabsorption. The main point, however, is that the fluorescence lifetime is temperature independent, and long compared to the measured high temperature (>4 K) dephasing rates. The fixed delay measurements at low temperature allow extraction of pure dephasing lifetimes without any other prior knowledge of the fluorescence lifetime than that it is temperature independent. Note that in the temperature range from 1.5–20 K the homogeneous linewidth changes from 7 MHz to 5 cm^{-1} (1.5×10^5 MHz). The upper part of Fig. 6 shows the temperature dependence of the homogeneous

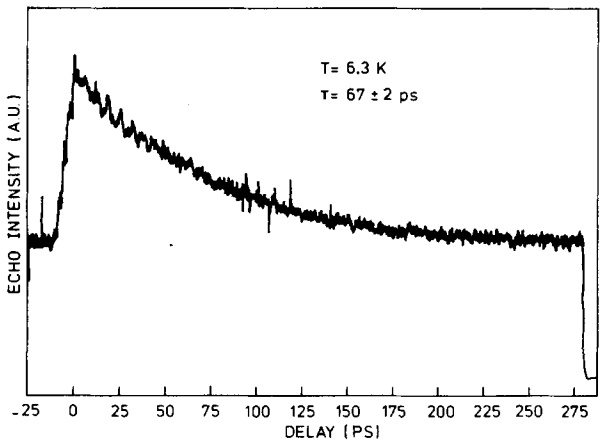

FIG. 5. Photon echo decay at 6.3 K of the zero-phonon line of photosite I of pentacene in benzoic acid. At a delay of 280 ps the pump beam was blocked to determine the incoherent background contribution to the signal (Ref. 12).

width of the librational transition at 16.7 cm^{-1} from the origin.

The first thing to note is that as long as the linewidth of the librational transition remains constant, the linewidth of the origin exhibits a quasiexponential activation, indicated by the dashed line in Fig. 6, with an activation energy of 14.0 cm^{-1} and preexponential constant of 1.5 cm^{-1}. This activation energy is close to the average of the librational frequency in the ground and excited state

$$(12.0 + 16.7)/2 = 14.3\ cm^{-1},$$

which indicates that *both* librations are involved in the dephasing process. The second point is that at low temperature the activation energy is distinctly lower than 14.0 cm^{-1}, as expected from the UPS mechanism. According to Eq. (2) at low temperature the lowest frequency libration will dominate the dephasing process. The solid line going over into the dotted line in Fig. 6 is the best fit to Eq. (2), where $\tau_4(T)$ is obtained from the T_1 contribution of the homogeneous linewidth of the librational transition (*vide infra*) and τ_3^{-1} ($T = 0$ K) is an adjustable parameter. From this fit the low-temperature lifetime of the pentacene libration in the ground state is found to be 18 ± 2 ps, which is to be compared with the 2.5 ps lifetime of this mode in the excited state. The fit between the experimental results and the theoretical expression in Eq. (2) can even be made perfect as shown by the solid line by adding to τ_3^{-1} ($T = 0$ K) a temperature dependent part, where we assume that the broadening of the ground state libration is similar to that of the excited state.

The solid line in Fig. 7 is also a fit to Eq. (2) with the parameters just mentioned. In this temperature range, however, optical dephasing is dominated by phonon scattering to the ground state librational mode (12 cm^{-1}) and consequently a fit to a single exponential activation with a 12 cm^{-1} activation energy is also possible. The preexponential constant of 0.5 cm^{-1} obtained in this latter fit is not directly interpretable in terms of a lifetime as this constant includes effects of the excited state librational mode which was neglected.

To conclude this section, we emphasize that the homogeneous line shape of the pentacene transition in this site up to 20 K can be explained on the basis of a dephasing mechanism where uncorrelated phonon scattering processes occur

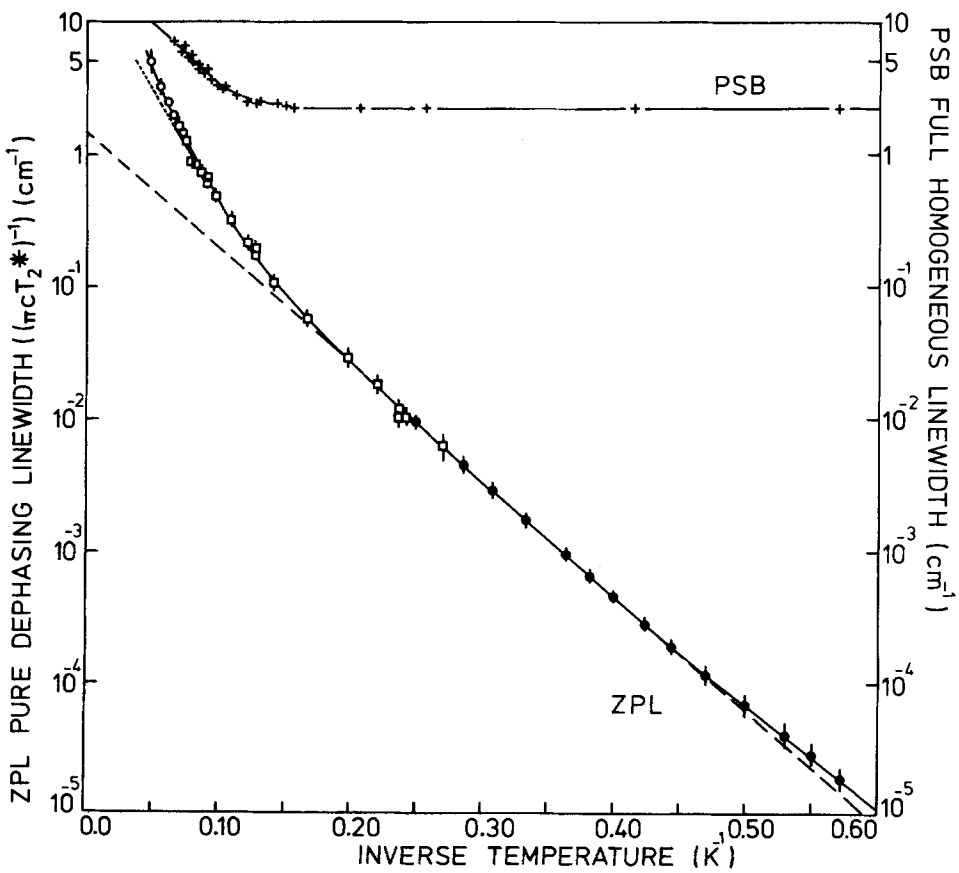

FIG. 6. The lower curve presents the pure dephasing contribution to the homogeneous linewidth of the zero-phonon line of photosite I of pentacene in benzoic acid. The data points represented by open circles were obtained from a line shape analysis. The points indicated by open squares were obtained from photon echo decay measurements at a fixed temperature. The filled circles were deduced from a measurement of the photon echo intensity at a fixed (3.37 ns) delay between the excitation pulses. The upper curve gives the homogeneous width of the libronic transition 16.7 cm^{-1} to the blue of the zero-phonon line. The fits to the upper and lower curves are discussed in the text.

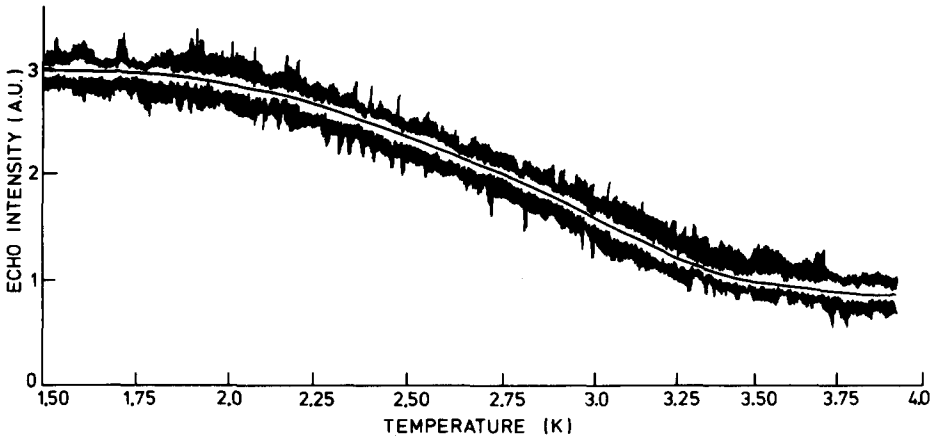

FIG. 7. Accumulated echo intensity as a function of temperature at a fixed delay of 3.37 ns. The solid line, which is the fit to the intensity change, is discussed in the text.

in the ground and excited state. The only *ad hoc* assumption made is that the ground state libration exhibits a similar temperature dependence as the excited state libration. This point is further discussed in Sec. D.

Finally we note that if the exchange equation (3) is used to fit the data in the region up to 5 K, as given by the dashed line in Fig. 6, we calculate from the preexponential constant of 1.5 cm^{-1} and $\delta/2\pi = 4.7$ cm^{-1} a librational lifetime of 6.9 ps. This number is in disagreement with the measured librational lifetime of 2.5 ps in the excited state and inferred lifetime of 18 ps in the ground state. The 6.9 ps lifetime, however, is close to the *average* librational lifetime of

$$(2.5 + 18)/2 = 10.25 \text{ ps}.$$

D. Librational dephasing and relaxation

The homogeneous width of a libronic transition in optical spectra is, as in the case of the pure electronic transition, determined by population relaxation (T_1) and pure dephasing (T_2^*) effects. At low temperature the pure dephasing contribution to the homogeneous width will be negligible and it is therefore justified to calculate from this width the low-temperature librational lifetime. With increasing temperature, however, dephasing processes are known to become important and the homogeneous width will be the sum of both. In the dBW optical dephasing model [Eq. (2)] the temperature dependent librational lifetimes are important parameters and need to be known. In order to extract from a linewidth measurement on a libronic transition the part only caused by population decay we need information on the dephasing of this transition. In complete analogy to the pure electronic transition we can write for the pure dephasing contribution to the homogeneous width of the libronic transition the following:

$$\frac{1}{T_2^*} = \tfrac{1}{2}(\tau_3^{-1}(T)e^{-\hbar\omega_{31}/kT} + \tau_6^{-1}(T)e^{-\hbar\omega_{64}/kT}). \quad (4)$$

Here $\tau_3(0)$ is the 18 ps lifetime of the libration in the ground state and $\tau_6(0)$ the 1.2 ps lifetime (cf. Sec. E) of the doubly excited librational level in the excited state at low temperature. Furthermore, ω_{31} equals the 12 cm^{-1} frequency of the ground state libration and ω_{64} represents 16.7 cm^{-1} energy difference between the doubly and singly excited librational state. We have calculated, using Eq. (4) and the quoted low-temperature librational parameters, the pure dephasing contribution to the homogeneous linewidth of the libronic transition. This turns out, in the temperature region of interest, never to exceed 10% of the homogeneous width. This fact has kept us from trying to include in the calculation the temperature dependence of the libronic lifetime (*vide infra*). This omission has little effect on the calculation of the libronic lifetime and *no* effect on the best fit in Fig. 6. By subtracting this calculated dephasing width from the measured homogeneous width presented in Fig. 6, the T_1 contribution to the linewidth can be obtained. From this width it is a trivial matter to obtain the upper limit (*vide supra*) of the temperature dependent librational lifetime [$\tau_4(T)$] as displayed in Fig. 8.

We first note that the temperature dependence of the librational lifetime is much steeper than observed for the lowest-frequency libron in pure naphthalene.[26] In addition, the low-temperature lifetime of this pentacene libration is a factor of 100 shorter than the lowest-frequency naphthalene libration.

The lifetime of a pseudolocalized libration is determined by libration-phonon scattering processes of which the dominant terms are given by[10]

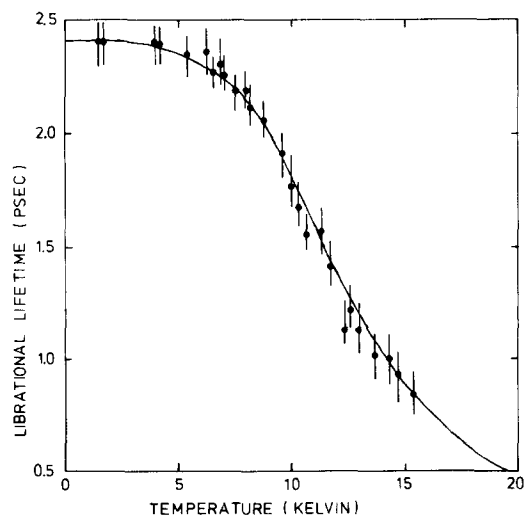

FIG. 8. Librational lifetime as a function of temperature. The data points were obtained from the upper curve in Fig. 6 by using Eqs. (2) and (5). The solid line is a fit of the form given by Eq. (10) with parameters mentioned in the text.

$$V_{1-p} = \sum_{\kappa} U_{\kappa\lambda}(b_{\kappa}^{+}B + b_{\kappa}B^{+}) + \frac{1}{3!}\sum_{\kappa\kappa'} U_{\kappa\kappa'\lambda}(b_{\kappa}b_{\kappa}^{+}B^{+} + b_{\kappa}b_{\kappa'}B^{+} + \text{c.c.}). \quad (5)$$

In Eq. (5) $b_{\kappa}^{+}(b_{\kappa})$ and $B_{\kappa}^{+}(B_{\kappa})$ are the creation (annihilation) operators for the lattice phonon and the libration, respectively. The index λ is used where a libration is involved. $U_{\kappa\lambda}$ is the harmonic interaction between the libration and the host modes; $U_{\kappa\kappa'\lambda}$ is the well-known cubic interaction term, leading to up- and down-conversion processes. Thus, the first term in V_{1-p} describes the harmonic mixing between the crystal (acoustic) normal modes and the pseudolocalized molecular libration and leads to resonant decay of the libration.[27] As the acoustic phonon density of states forms a quasicontinuum at the librational frequency we may employ Fermi's golden rule to calculate the resulting resonant decay rate Γ_{res}^{l}:

$$\begin{aligned}\Gamma_{\text{res}}^{l} &= \frac{2\pi}{\hbar}\sum_{\kappa}(|\langle(l-1)_{\lambda},(n_{\kappa}+1)|b_{\kappa}^{+}B|l_{\lambda},n_{\kappa}\rangle|^{2} \\ &\quad - |\langle l_{\lambda},(n_{\kappa}-1)|B^{+}b_{\kappa}|(l-1)_{\lambda},n_{\kappa}\rangle|^{2})|U_{\kappa\lambda}|^{2}\rho_{\kappa}(\epsilon_{\lambda}) \\ &= \frac{2\pi}{\hbar}\sum_{\kappa} l(|\langle 0_{\lambda},(n_{\kappa}+1)|b_{\kappa}^{+}B|1_{\lambda},n_{\kappa}\rangle|^{2} \\ &\quad - |\langle 1_{\lambda},(n_{\kappa}-1)|B^{+}b_{\kappa}|0_{\lambda},n_{\kappa}\rangle|^{2})|U_{\kappa\lambda}|^{2}\rho_{\kappa}(\epsilon_{\lambda}) \\ &= l\frac{2\pi}{\hbar}\sum_{\kappa}|U_{\kappa\lambda}|^{2}\rho_{\kappa}(\epsilon_{\lambda}). \end{aligned} \quad (6)$$

Γ_{res}^{l} presents the decay rate from the librational level with l quanta to $(l-1)$, and n_{κ} is the occupation number of a lattice phonon with wave vector κ. $\rho_{\kappa}(\epsilon_{\lambda})$ is the phonon density of states at the energy ϵ_{λ} of the singly occupied libration. This expression shows that librational decay proceeds in single quantum steps down the librational ladder leading to a resonant decay rate that increases linearly with the librational quantum number l.

The second term in Eq. (5) represents the cubic-anharmonic libration-phonon interaction which leads to phonon up- and down-conversion processes. Using again Fermi's golden rule we come to the following contribution to the librational relaxation rate:

$$\begin{aligned}\Gamma_{\text{anh}}^{l} &= l\frac{2\pi}{\hbar}\sum_{\kappa\kappa'}\frac{18}{(3!)^{2}}|U_{\kappa\kappa'\lambda}|^{2}\rho_{\kappa\kappa'}(\epsilon_{\lambda}) \\ &\quad\times[\{(1+n(\epsilon_{\kappa})+n(\epsilon_{\kappa'}))\delta(\epsilon_{\lambda}-(\epsilon_{\kappa}+\epsilon_{\kappa'}))\} \\ &\quad+\{2(n(\epsilon_{\kappa})-n(\epsilon_{\kappa'}))\delta(\epsilon_{\lambda}-(\epsilon_{\kappa'}-\epsilon_{\kappa}))\}]. \end{aligned} \quad (7)$$

Here $\rho_{\kappa\kappa'}(\epsilon_{\lambda})$ stands for the two-phonon density of states at ϵ_{λ} for up-

$$\left(\rho_{\kappa\kappa'}(\epsilon_{\lambda}) = \int_{0}^{\epsilon_{\lambda}}\rho_{\kappa}(\epsilon)\rho_{\kappa'}(\epsilon-\epsilon_{\lambda})d\epsilon\right)$$

and down-

$$\left(\rho_{\kappa\kappa'}(\epsilon_{\lambda}) = \int_{0}^{\epsilon_{\lambda}}\rho_{\kappa}(\epsilon)\rho_{\kappa'}(\epsilon_{\lambda}-\epsilon)d\epsilon\right)$$

conversion, respectively. In contrast to harmonic decay $(\Gamma_{\text{res}}^{l})$, Γ_{anh}^{l} is temperature dependent through the Bose–Einstein occupation numbers

$$n(\epsilon_{\kappa}) = (\exp(\hbar\omega_{\kappa}/kT)-1)^{-1}.$$

Note again that with the chosen anharmonic phonon terms, librational decay proceeds in single quantum steps down the librational ladder and also that Γ_{anh}^{l} is proportional to l. The librational lifetime τ_{l} resulting from these phonon-scattering processes is related to the sum of Γ_{res}^{l} and Γ_{anh}^{l} in the following way:

$$\tau_{l}^{-1} = \Gamma_{\text{res}}^{l} + \Gamma_{\text{anh}}^{l} = l(\Gamma_{\text{res}}^{1} + \Gamma_{\text{anh}}^{1}). \quad (8)$$

Fischer[28] has shown that other anharmonic phonon interactions give a negligible contribution to the librational lifetime. For example, direct communication between the doubly excited librational level and its ground state (of the type

$$\langle 2_{\lambda}m_{\kappa}|b_{\kappa}B^{+}B^{+}|0_{\lambda}(m+1)_{\kappa}\rangle + \text{c.c.})$$

is not efficient because the phonon density of states involved in the golden rule equation for this process is much lower than that for the processes of Eq. (5).

We are now in a position to analyze the librational lifetime data, presented in Fig. 8, in terms of different libration-phonon interactions. The solid line in Fig. 8 is a theoretical fit to the sum of the harmonic and anharmonic relaxation rates of the form

$$\tau_{4}(T)^{-1} = \Gamma_{\text{res}}^{1} + |V_{d}|^{2}(2n(\tfrac{1}{2}\epsilon_{\lambda})+1) + |V_{u}|^{2}(n(\epsilon_{s}-\epsilon_{\lambda})-n(\epsilon_{s})) \quad (9)$$

with the following parameters:

$$\Gamma_{\text{res}}^{1} = 1.9\ \text{cm}^{-1},\quad \begin{aligned}|V_{d}|^{2} &= 0.3\ \text{cm}^{-1},\ \epsilon_{\lambda} = 16.7\ \text{cm}^{-1}\\ |V_{u}|^{2} &= 80\ \text{cm}^{-1},\ \epsilon_{s} = 50\ \text{cm}^{-1}.\end{aligned}$$

Here the summations in Eqs. (6) and (7) are approximated by the leading terms.[26] $|V_{d}|^{2}$ stands for the effective matrix element in the down-conversion process, $|V_{u}|^{2}$ for that involved with up-conversion. We first note that at 0 K only Γ_{res}^{1} and $|V_{d}|^{2}$ contribute to the linewidth. The relative importance of these terms can be derived from the low-temperature curvature of the linewidth, which makes an accurate determination of the resonant decay and down-conversion processes possible. The resulting parameters used in the fit show that *resonant* decay is the most important one at low temperature. The fit turns out to be rather insensitive to the choice of ϵ_{s} in the up-conversion process; a larger value of ϵ_{s} can be compensated by a larger $|V_{u}|^{2}$ to maintain a good fit. Irrespective of the precise magnitude of $|V_{u}|^{2}$ it is clear that the cross section for up-conversion far exceeds that of down-conversion as in the case of libron decay in pure naphthalene.[26]

With the assumption that the decay of the libration in the ground state of pentacene is affected by similar processes as in the excited state, we can simulate its temperature dependence. The actual best fit to the linewidth data in Fig. 6 was made with the following parameters for $\tau_{3}(T)^{-1}$:

$$\Gamma_{\text{res}}^{1} = 0.26\ \text{cm}^{-1},\quad \begin{aligned}|V_{d}|^{2} &= 0.04\ \text{cm}^{-1},\ \epsilon_{\lambda} = 12.0\ \text{cm}^{-1}\\ |V_{u}|^{2} &= 80\ \text{cm}^{-1},\ \epsilon_{s} = 50\ \text{cm}^{-1}.\end{aligned}$$

These parameters were chosen such that the relative ratio of $|V_{d}|^{2}$ and Γ_{res} are the same as in the excited state and furthermore that the doorway state in the up-conversion process is the same as in the excited state.

E. Optical dephasing induced by librational overtones

One of the pertinent questions to ask is why at elevated temperature optical dephasing still is describable in terms of a four-level model. First of all there is no *a priori* reason why other librations should not play a role in the dephasing mechanism. Therefore, in the most general case Eq. (2) should include a sum over all singly excited librational levels of the molecule. The reason that, in the pentacene case, no other librations seem to play a role in the dephasing process must be that these other librations are of much higher frequency and therefore do not contribute in the temperature range of our studies.

A more serious question concerns the role of librational overtones in the dephasing process. For photosite I of pentacene in benzoic acid the homogeneous width of the optical transition to the librational overtone at 33.3 cm^{-1} from the origin is, again assuming a 1.0 cm^{-1} inhomogeneous contribution 4.4 ± 0.2 cm^{-1} which is due to a 1.2 ps librational lifetime. If such a state is dealt with on equal footing as the fundamental libration in Eq. (2) the effect of this state would add substantially to the width of the optical transition at temperatures above 10 K. The reason that these states should not be incorporated in the dephasing model stems from the fact that in the Redfield dephasing theory, as developed by de Bree and Wiersma, for the UPS case,[10] the dephasing rate for the optical transition is the sum of the scattering rates *out* of the initial and final states. For phonon scattering processes from these levels to the singly excited libration states these rates are, by the condition of detailed balance, directly connected to the lifetime of the librational levels. This detailed balance argument does not apply to scattering processes that involve higher excited librational levels as they may not directly relax to the librational ground state. In fact Eqs. (6) and (7) show that for the libration-phonon interaction term in V_{l-p} librational overtones only relax down the librational ladder, in single quantum steps. A strong argument in favor of this idea is given by the fact that the homogeneous width of the librational overtone 4.4 ± 0.2 cm^{-1} is twice the homogeneous width of the fundamental libronic transition in the optical spectrum. In this situation the upward scattering rate to these overtones equals zero and no contribution of these states to optical dephasing is expected. The conclusion of this section therefore is that multiply excited librational states will have *no effect* on the homogeneous line shape of the zero-phonon line.

F. Relevance to previous experiments on the unburned origin

With our present understanding of the mechanism for dephasing in the zero-phonon line of photosite I of pentacene in benzoic acid it seems relevant to return to the problem of dephasing in the unburned origin. As mentioned in the Introduction the situation for the unburned origin is somewhat confusing as different activation energies for the homogeneous width[14,16,17] have been reported. When the temperature-activated homogeneous width of the unburned origin previously reported by our group[14] is compared to that of photosite I up to 20 K, hardly any difference between the two is noticeable. We therefore propose that the dephasing mechanism for the two is the same, with a small change in librational parameters. The hole burning results reported by Olson *et al.*,[16] showing an activation of the low-temperature homogeneous width by 11 cm^{-1}, can be interpreted as reflecting primarily phonon scattering in the ground state involving a 11 cm^{-1} libration. The preexponential constant of 0.3 cm^{-1} obtained from these low-temperature hole burning data also suggests a long lifetime of the libration in the ground state. As a single exponent was used to fit the data it is obviously incorrect to directly relate this number to a lifetime. Further support for assuming the dephasing mechanisms to be identical comes from the fact that the low-temperature photon echo data of the *unburned* origin (Fig. 3 of Ref. 14) can also be interpreted using an 11 cm^{-1} activation energy. The transition at 33.8 cm^{-1} from the origin in emission in the unburned origin then should be correlated to the 33 cm^{-1} transition observed for photosite I, rather than being interpreted as the overtone of a 16.9 cm^{-1} ground state libration as suggested previously.[14] Finally, the activation energy of 13.8 cm^{-1}, obtained by Andrews and Hochstrasser[17] from a coherent Raman study on the unburned origin, is close to the average librational frequency of

$$(16.4 + 11)/2 = 13.7 \text{ cm}^{-1}$$

in this transition. We can not, however, reconcile their preexponential factor to the librational lifetimes and suspect that this factor must contain contributions from other sources. The interesting conclusion therefore is that the proton rearrangements responsible for photosite I in the benzoic acid crystal have little effect on the frequency and lifetime of the guest libration. The most dramatic effect is seen in the intensities of the phonon sidebands and indicates that the site symmetry has changed in the proton rearrangement process.

V. EPILOGUE

The results given in this paper present definite proof that in the mixed crystal of pentacene in benzoic acid, optical dephasing proceeds via uncorrelated phonon scattering processes with singly occupied librational levels. In the system pentacene in naphthalene the same mechanism was proposed,[18] but direct measurement of the librational lifetime was impossible. In both cases it was found that the librational lifetime was rather different in the ground and excited states. It is exactly this point which makes exchange of optical coherence in these transitions an unlikely event. In fact the only well-documented case of coherence exchange in an optical transition presents the Sphol'skii system free-base porphin in *n*-octane.[5] Another exceptional case is the mixed crystal of triphenylmethyl in triphenylamine where neither coherence exchange nor UPS processes involving a libration are involved in optical dephasing. The obvious reason for this anomaly is the fact that the guest is so similar to the host that the guest librations are amalgamated into the host libron bands. For this system adiabatic coupling to host acoustic phonons, leading to a T^7 dependence for the homogeneous linewidth, was found to dominate optical dephasing.[29]

It remains interesting to speculate on the reason for the different behavior of free-base porphin in *n*-octane com-

pared to all other "aromatic"-type mixed crystals studied so far.[29] It is clear that, in order to observe coherence exchange effects the librational potential must be little affected by optical excitation.

In aromatic-type mixed crystals the guest–host interaction is quite substantial as evidenced by the gas-to-crystal shift which can amount to several hundreds of wave numbers. In Shpol'skii matrices on the contrary the guest–host interaction leads only to minor spectral shifts of the optical transition. Even and Jortner[30] recently reported for free-base porphin a gas-to-Shpol'skii shift of only tens of wave numbers. The different behavior of Shpol'skii matrices compared to the aromatic host crystals must be attributed to the difference in polarizibility of these compounds. We therefore conclude that the likelihood for the observation of coherence exchange in optical transitions is maximal in those systems where the "cage polarizibility" is small. Next to Shpol'skii matrices also the noble-gas matrices seem to be good candidates for the observation of optical exchange.

In the case of pure vibrational excitations in either an aromatic or Shpol'skii host the librational potential is little affected and the librational frequency in the ground and excited states is nearly identical. In this extreme limit of exchange theory [$\delta \approx 0$ in Eq. (3)], vibrational dephasing by molecular librations is blocked. This effect was recently demonstrated for vibrational transitions of pentacene in naphthalene and benzoic acid.[13]

We end by noting that librational decay at low temperature in the mixed crystal of pentacene in benzoic acid is dominated by direct decay into host acoustic modes. It remains to be seen whether this presents an exceptional case or that in other mixed crystals, like in pure crystals,[26,27] cubic libration-phonon anharmonicity determines the librational lifetime.

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[1] D. S. McClure in *Electrical Conductivity in Organic Solids*, edited by H. Kallman and M. Silver (Interscience, New York, 1961).
[2] T. R. Koehler and J. Schmidt, Chem. Phys. Lett. **75**, 38 (1980).
[3] C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. **36**, 457 (1975).
[4] T. J. Aartsma and D. A. Wiersma, Chem. Phys. Lett. **42**, 520 (1976).
[5] S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, J. Chem. Phys. **67**, 1759 (1977); S. Völker, R. M. Macfarlane and J. H. van der Waals, Chem. Phys. Lett. **53**, 8 (1978).
[6] C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. **36**, 460 (1975); **42**, 73 (1976).
[7] G. J. Small, Chem. Phys. Lett. **57**, 501 (1978).
[8] C. B. Harris, J. Chem. Phys. **67**, 5607 (1977).
[9] K. E. Jones and A. H. Zewail in *Advances in Laser Chemistry*, edited by A. H. Zewail (Springer, Berlin, 1978).
[10] Ph. de Bree and D. A. Wiersma, J. Chem. Phys. **70**, 790 (1979); Ph. de Bree, Ph. D. Thesis, University of Groningen, The Netherlands, 1981.
[11] I. I. Abram, Chem. Phys. **25**, 87 (1977).
[12] W. H. Hesselink and D. A. Wiersma in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North–Holland, Amsterdam, 1983).
[13] K. Duppen, D. P. Weitekamp, and D. A. Wiersma, J. Chem. Phys. **79**, 5835 (1983).
[14] K. Duppen, L. W. Molenkamp, J. B. W. Morsink, D. A. Wiersma, and H. P. Trommsdorff, Chem. Phys. Lett. **84**, 121 (1981).
[15] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).
[16] R. W. Olson, H. W. H. Lee, F. G. Patterson, M. D. Fayer, R. M. Shelby, R. M. Macfarlane, and D. P. Burum, J. Chem. Phys. **77**, 2283 (1982).
[17] J. R. Andrews and R. M. Hochstrasser, Chem. Phys. Lett. **82**, 381 (1981).
[18] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. **73**, 648 (1980).
[19] H. B. Levinsky and D. A. Wiersma (unpublished results).
[20] M. Wagner, Z. Naturforsch. Teil A **14**, 81 (1959).
[21] T. R. Koehler, Mol. Liq. Cryst. **50**, 93 (1979); J. Chem. Phys. **72**, 3389 (1980).
[22] R. Silbey, H. P. Trommsdorff, and D. A. Wiersma (unpublished results).
[23] A. I. M. Dicker, J. Dobkowski, and S. Völker, Chem. Phys. Lett. **84**, 415 (1981).
[24] B. T. Thole (private communication).
[25] D. P. Weitekamp, K. Duppen, and D. A. Wiersma, Phys. Rev. A **27**, 3089 (1983).
[26] K. Duppen, H. M. M. Hesp, and D. A. Wiersma, Chem. Phys. Lett. **79**, 399 (1981).
[27] See, for example: A. A. Maradudin in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966) Vols. 18 and 19. For applications to molecular crystals we refer to: G. J. Small, J. Chem. Phys. **58**, 2015 (1973); and P. N. Prasad and R. Kopelman, *ibid.* **58**, 5031 (1973).
[28] G. Fischer, Chem. Phys. **16**, 181 (1976).
[29] W. H. Hesselink and D. A. Wiersma, Chem. Phys. Lett. **50**, 51 (1977); D. A. Wiersma in *Photoselective Chemistry*, edited by J. Jortner (Wiley, New York, 1981).
[30] U. Even and J. Jortner, J. Chem. Phys. **77**, 4391 (1982).